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Synthesis and Characterization of PCL-*b*-PEO-*b*-PCL-Based Nanostructured and Porous Hydrogels

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Hydrogels with nanoscale structure were synthesized using amphiphilic poly(ϵ-caprolactone)−poly(ethylene oxide)−poly(ϵ-caprolactone) (PCL-*b*-PEO-*b*-PCL) triblock copolymers. Small-angle X-ray scattering (SAXS) studies show that the block copolymers form 30−40 nm structures in aqueous solution and that these patterns are retained, with some increase in length scale, following electron beam cross-linking. Lamellar nanostructures were observed by SAXS and atomic force microscopy (AFM), with SAXS indicating cylindrical structure as the block lengths become more different in length. It is demonstrated through Fourier transform infrared spectroscopy (FTIR), mass loss, and differential scanning calorimetry (DSC) that the PCL can be completely removed by hydrolysis in NaOH(aq) to form porous PEO hydrogels. These hydrogels retain active functional groups following PCL removal that serve as sites for further chemical modification.

Introduction

Nanoporous materials have received much attention due to their well-ordered nanoscale pore structures and their high surface areas and have been studied for numerous potential applications in separation, catalysis, nanolithography, and as low dielectric materials. While inorganic nanoporous materials synthesized with metal oxides are hydrophilic, the majority of current nanoporous organic materials are hydrophobic, which limits potential biomedical applications. In this study, we report a novel synthetic method for hydrophilic, flexible, nanostructured, and porous polymer networks.

Nanoporous materials derived from block copolymers are advantageous for the degree of control over pore size distribution that they offer. These materials are synthesized by connecting two or more chemically distinct polymer blocks, inducing microphase separation to form a pattern on the length scale of tens of nanometers, and removing one of polymer blocks to generate voids. Polymers with high glass transition temperatures (T_g) have been used for the nondegradable blocks because a high T_g offers retention of structure at mild temperatures despite the absence of chemical cross-links.[1−3] However, once the glass melts or contacts a good solvent, such porosity disappears. This problem can be avoided by cross-linking a nondegradable block as shown by Lee et al.[4] and Cavicchi et al.[5]

Amphiphilic polymer networks (APNs) have been studied extensively for biological applications due to the presence of both hydrophilic and hydrophobic domains.[6] Specifically, Barakat et al.[7] synthesized APNs using block copolymers of polyester and poly(2-hydroxyethyl methacrylate) (PHEMA) and studied hydrophilic and hydrophobic drug release profiles as the networks are swollen in hydrophilic and hydrophobic solvents. Another recent example is a poly(ethylene oxide)−poly(dimethyl siloxane) (PEO−PDMS) network that can be used in contact lenses due to its optical clarity when swollen in water and to its high oxygen permeability.[8] Hentze et al.[9] also used PEO as a hydrophilic domain in their study of a PEO-*b*-poly(butadiene) network. They induced microphase separation of the diblock copolymer in water to produce lamellar and cylindrical microstructures and then fixed the ordered structures by ^{60}Co radiation-induced cross-linking. In our study, an APN system is used to produce nanostructures in water, but instead of using the hydrophobicity of the hydrophobic domain as in the examples above, it is removed to produce a nanoporous hydrophilic network.

In this study, PCL-*b*-PEO-*b*-PCL block copolymers were selected. As shown by Bae et al.,[10] these block copolymers show different microstructures by micellization in water depending upon the polymer concentration[11] and the temperature. The molecular weights of the blocks also affect the phase structure.[12] The copolymers must be cross-linked prior to void formation in order to retain any spatial structure originating from block copolymer templating. PEO can be cross-linked by an electron beam,[13] by UV,[14] or by a ^{60}Co source.[15−17] Here, an electron beam is used to cross-link the polymer through covalent C−C bonds such that the resulting cross-links do not degrade once the PCL blocks are removed through hydrolysis of PCL's ester linkages in NaOH(aq)[3]. The terminal hydroxyl groups of PEO are restored after the PCL is removed through hydrolysis, allowing later chemical modification. Due to their hydrophilicity and biocompatibility, the resulting nanoporous PEO networks may find use as hydrogels for selective separation or drug delivery.

Experimental Section

Materials. PEO, ϵ-caprolactone, and stannous octoate were purchased from Sigma-Aldrich and used without further purification. PEO-*b*-PCL diblock copolymer (M_n = 5000−4000 g/mol) was purchased from Polymer Source (Quebec, Canada). Sodium azide and methanol were purchased from Mallinckrodt (Phillipsburg, NJ), and the solvents (dichloromethane, *n*-hexane) were obtained from EMD Chemicals (Gibbstown, NJ).

Synthesis of PCL-*b*-PEO-*b*-PCL Triblock Copolymers. PEO was reacted with ϵ-caprolactone in the presence of stannous octoate as a catalyst at 130 °C for 21 h under a nitrogen atmosphere. Synthesized

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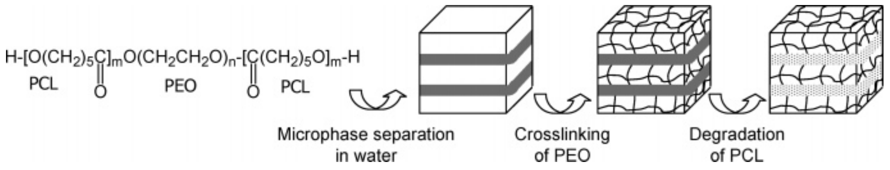
Scheme 1. Synthesis of Nanostructured and Porous Hydrogel



$H-[O(CH_2)_5C(=O)]_mO(CH_2CH_2O)_n-[C(=O)(CH_2)_5O]_m-H$

Table 1. PCL-*b*-PEO-*b*-PCL Triblock Copolymers Synthesized

	M_n (PEO) g/mol[a]	M_n (NMR) g/mol[b]	M_n g/mol[c]	M_w/M_n[c]	polymerization yield (%)[d]
poly1	15 000	7500−15 000−7500	29 000	1.23	58
poly2	30 000	9000−30 000−9000	43 000	1.17	33
poly3	47 000	19 000−47 000−19 000	36 000	2.55	46

[a] Determined by GPC using starting PEO homopolymer. [b] Determined by ^{1}H NMR based on the M_n of PEO measured by GPC. [c] From GPC. [d] Determined by comparing the amount of added ϵ-CL monomer and the M_n (NMR) of the PCL block.

block copolymers were dissolved in dichloromethane and precipitated into cold *n*-hexane three times to remove unreacted monomers, and the final products were dried in a hood at room temperature for 1 day and in a vacuum oven at 40 °C for another 2 days. Three different triblock copolymers were synthesized using different molecular weights of the PEO macroinitiator.

Cross-Linking of PCL-*b*-PEO-*b*-PCL by Electron Beam Irradiation. PCL-*b*-PEO-*b*-PCL was dissolved in Milli-Q water in a Petri dish 5 cm in diameter, with 0.01% NaN_3 added to retard bacterial growth. After equilibrating the aqueous solutions at room temperature for 1 week, electron beam irradiation was carried out at the High Voltage Research Laboratory (HVRL) at MIT, using a 2.5 MeV van de Graff generator with a dose rate of 1.25 Mrad/pass and a belt speed of 0.8 cm/s. The temperature was not controlled during irradiation. For an emulsion at 20% polymer concentration, a 30 Mrad dose was used, while 50 Mrad doses were used at 40%, 60%, and 80% polymer concentrations. The maximum film thickness achievable with little depth variation in the electron dose is ∼0.5 cm,[13] and our samples were approximately 0.2 cm thick. After cross-linking, the samples were extracted with 0.01% NaN_3 Milli-Q water, and the final products were dried in a vacuum oven at 40 °C for 2 days. Dry weights of samples before and after extraction were compared to calculate the gel fractions.

Synthesis of Nanostructured and Porous PEO Hydrogel. Cross-linked samples of PCL-*b*-PEO-*b*-PCL were placed in 40/60 (v/v %) methanol/water solutions with 0.5 M NaOH at 100 °C for 2 days to hydrolyze the ester linkages of the PCL blocks. The degradation was followed by extraction with 40/60 (v/v %) methanol/water solutions and pure water to remove the degraded PCL monomer and oligomer segments. The final products were dried in a vacuum oven at 40 °C for 2 days.

Esterification of the Nanostructured and Porous PEO Hydrogel. The porous PEO hydrogels produced by the PCL degradation were reacted with an excess amount of glutaric acid at 100 °C for 1 h in the presence of concentrated sulfuric acid as a catalyst and 3 Å molecular sieves for absorption of the water byproduct. As a reference sample in which no esterification was to be expected, the same reaction condition was used except that toluene was added instead of glutaric acid. The reacted PEO hydrogels were extracted with dichloromethane and water.

Characterization. Number- and weight-average molecular weights (M_n and M_w, respectively) and polydispersities (M_w/M_n) were obtained with a Waters gel permeation chromatograph (GPC) at the University of Akron using tetrahydrofuran (THF) as the solvent at a 1 mL/min elution rate with calibration through use of polystyrene standards. Proton nuclear magnetic resonance (^{1}H NMR) spectra were acquired by a 300 MHz Varian Mercury apparatus using $CDCl_3$ as a solvent at the MIT Department of Chemistry Instrumentation Facility (DCIF). Small-angle X-ray scattering (SAXS) experiments were performed at the Institute for Soldier Nanotechnologies (ISN) at MIT, and ultrasmall-angle X-ray scattering (USAXS) was conducted by a University−National Laboratory−Industry collaborative access team (UNICAT) at the Argonne National Laboratory. Wet samples of triblock copolymers (emulsions in water, cross-linked polymer hydrogels, and porous hydrogels after PCL removal) were enclosed or mounted upon Kapton tape. SAXS data were collected for exposures of 1000 s at room temperature. Background calibration was performed by subtracting the signals from the corresponding empty Kapton tape holders. Atomic force microscopy (AFM) images were taken with a Veeco Metrology Group Nanoscope IV scanning probe microscope (Digital Instruments) at the MIT Center for Material Science and Engineering (CMSE). Dry samples were microtomed to produce smooth surfaces for AFM measurement. Fourier transform infrared spectroscopy (FTIR) measurements were conducted using a Nicolet Magna 860 at CMSE. Samples for IR measurement were vacuum-dried at 40 °C for at least 2 days prior to analysis and prepared by the following methods: (1) by grinding a dried sample with a mortar and pestle and mixing with KBr powders, (2) by crushing a dry sample to form a thin film on a ZnSe plate, or (3) by making a thin film using diamond compression cell windows. Melting points (T_m) of block copolymers were obtained with a Perkin-Elmer Pyris 1 differential scanning calorimeter (DSC) at CMSE. Wet samples of 5−10 mg were used for DSC, and high-pressure stainless steel pans with O-rings were used to prevent evaporation of water. The samples were heated at the rate of 10 °C/min from 20 to 100 °C and cooled at the rate of 10 °C/min to 20 °C to erase prior thermal history. These samples were heated again to 100 °C at the same rate to collect the DSC results.

Results and Discussion

The synthetic route to produce the nanostructured and porous hydrogel is shown in Scheme 1. Amphiphilic PCL-*b*-PEO-*b*-PCL block copolymers are synthesized, which form different microstructures in water depending upon the polymer concentration and the block lengths (a lamellar phase is shown as an example). The copolymers must be cross-linked prior to void formation in order to retain any spatial structure originating from the block copolymer templating. The ordered emulsion is cross-linked by electron beam, as the resulting cross-links do not degrade when the PCL blocks are removed through hydrolysis of their ester linkages. The terminal hydroxyl groups of PEO are restored when the PCL is removed, allowing later chemical modification.

In the following, each step is described.

I. Synthesis of PCL-*b*-PEO-*b*-PCL Triblock Copolymers and Their Microphase Separation in Water. PEO was reacted with ϵ-caprolactone in the presence of stannous octoate as a catalyst. Hydroxyl groups of PEO react with the catalyst, and this complex initiates the ring opening polymerization of ϵ-caprolactone. Three different triblock copolymers were synthesized using different molecular weights of PEO macroinitiator, as shown in Table 1. Molecular weights and polydispersity indices of the synthesized triblock copolymers were

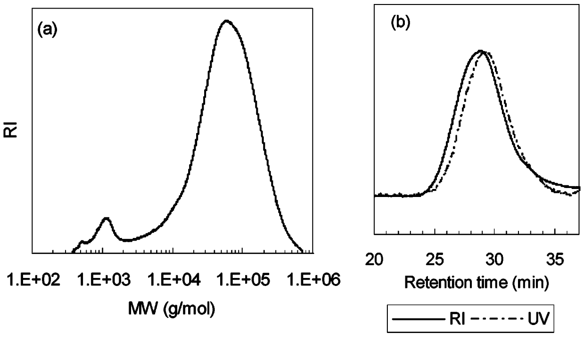


Figure 1. GPC of poly3; (a) molecular weight distribution and (b) chromatogram.

determined by GPC, and block lengths of PCL were determined by ^{1}H NMR. The triplet PCL peak at 4.067 ppm was compared with the singlet PEO peak at 3.651 ppm to determine the molecular weight of the PCL block.[18,19] The M_n of poly3 determined by GPC is lower than the M_n of the starting PEO homopolymer. This is perhaps due to degradation or may be related to the unusually high polydispersity and pronounced low-MW shoulder. Figure 1a shows the broad molecular weight distribution of poly3, including an additional small peak at very low molecular weights that was not observed for poly1 and poly2. The low-MW side peak suggests that poly3 contains degraded products of PEO or short PCL oligomers. The M_n reported in Table 1 was determined by considering the high molecular weight peak only. Comparison of the GPC curves for the refractive index (RI) and UV detectors shows poly3 to contain a considerable amount of triblock copolymer rather than merely homopolymers, as is shown in Figure 1b. Specific refractive index increments (d*n*/d*c*) of PEO and PCL in THF are comparable (0.068 mL/g[20] vs 0.0795 mL/g,[21] respectively at 546 nm). Therefore, the RI intensity (measured at 690 nm) in Figure 1b indicates signals from both PEO and PCL, whereas the ultraviolet (UV) peak measured at 250 nm detects mainly PCL due to its ester groups.[22] Although the RI and UV curves are not identical, their closely located peak positions indicate poly3 chains are mostly block copolymer.

Microphase separation of PCL-*b*-PEO-*b*-PCL triblock copolymers in water was achieved by equilibrating aqueous solutions of the triblock copolymers at room temperature for 1 week, and the resulting microstructures were observed by SAXS. Figure 2 shows SAXS spectra of poly1 at various polymer concentrations. When poly1 was dissolved in water at a concentration of 20%, the emulsion sample has a peak at 40 nm. As polymer concentrations increase, *d*-spacing values of the emulsions decrease to 40, 34, and 29 nm at 40%, 60%, and 80% concentrations, respectively. All SAXS peaks were analyzed as plots of intensity $\times$ q^2 vs q. Several peaks are recognized at high concentrations of 60% and 80%, and the q ratio between the three peaks is 1:2:3, indicating lamellar structure. The 80% emulsion of poly2 shows a different q ratio, near $1{:}\sqrt{3}{:}\sqrt{4}{:}\sqrt{7}$, suggesting cylindrical structure (Figure 3). This polymer sample will be further studied to produce porous materials with cylindrical pores.

II. Cross-Linking of PEO in PCL-*b*-PEO-*b*-PCL by Electron Beam Irradiation. Cross-linking was performed by electron beam irradiation of aqueous solutions of PCL-*b*-PEO-*b*-PCL triblock copolymers. Under an electron beam, water is degraded to produce $\cdot$OH and $O^{\bullet -}$ radicals that abstract hydrogen from the $-\mathrm{CH}_{2-}$ groups of PEO. As cross-links are formed by the combination of these $-{\cdot}\mathrm{CH}-$ radials, the presence of water accelerates cross-linking during irradiation.[13] The hydrophobic PCL is expected to be cross-linked less extensively as water plays such an important accelerative role. Gel fraction data after cross-linking show poly1 and poly3 to achieve near 100% gel fractions. In Figure 4, the gel fractions of the poly1 and poly3 that were synthesized in our lab are compared with that of a commercially available diblock copolymer, PEO-*b*-PCL 5000−4000 g/mol. In the election beam cross-linking of PEO homopolymer (M_n = 15 000 g/mol), the molecular weight between cross-links (M_c) from swelling experiments was found to be dependent upon the polymer concentration; an M_c of 2500 g/mol was obtained at 20% vs values of ∼4000 g/mol at 40% and 60% concentrations[23] (data not shown). If it is assumed that a similar M_c is obtained in the block copolymers, it is understandable why the diblock copolymer, 5000−4000 g/mol, shows a lower gel fraction than the triblock copolymers with longer PEO blocks. At 40% and 60% polymer concentrations, an M_c of 4000 g/mol means that there is on average only one cross-link in a PEO block of MW 5000 g/mol. However, the numbers of cross-links per PEO block of

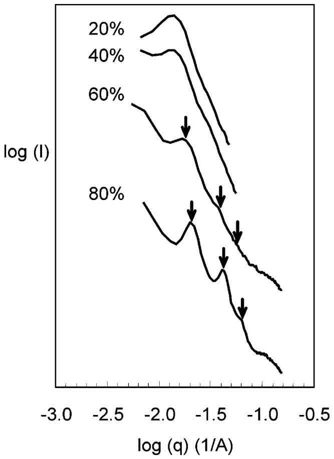


Figure 2. SAXS of poly1 at several concentrations in water; the arrows are expected peak positions for a lamellar microphase; the first-order peaks for 20%, 40%, 60%, and 80% are 40, 40, 34, and 29 nm, respectively.

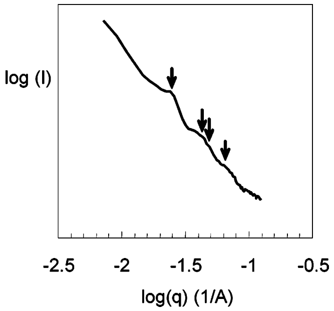


Figure 3. SAXS of poly2 at 80% in water; the arrows are expected peak positions for a cylindrical microphase; the first-order peak was observed at 25 nm.

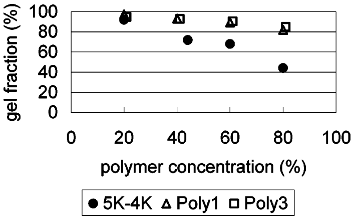


Figure 4. Gel fraction of block copolymers after electron beam cross-linking; 5K-4K denotes a commercially available PEO-*b*-PCL (M_n 5000−4000 g/mol).

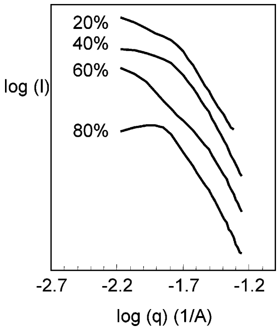


Figure 5. SAXS of poly1 after cross-linking in water; the first-order peaks for 20%, 40%, and 80% are 35, 37, and 40 nm, respectively.

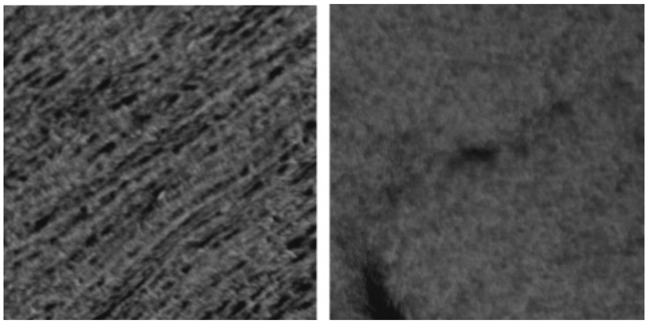
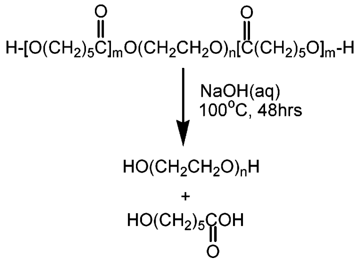


Figure 6. AFM phase images of the cross-linked polymers at 80% polymer concentration (dried sample): left, poly1 (lamellar structure, 27 nm); right, homopolymer PEO $M_n = 10\,000$ g/mol.

Scheme 2. Degradation of PCL in the PCL−PEO−PCL Triblock Copolymers



weights 15 000 and 47 000 g/mol are sufficiently greater than one to yield high gel fractions even at high polymer concentrations. Poly3 did not show a 100% gel fraction even though it has a long PEO block length, perhaps due to chain scission during electron beam irradiation.

Microstructures after cross-linking of the emulsions were observed by SAXS (Figure 5). Cross-linked samples were swollen in water, and SAXS measurements of these samples show that the microstructures originating from microphase separation in emulsions were retained with slight increases in length scales. The effects of cross-linking upon the morphology of the amphiphilic networks were also investigated by AFM. Figure 6 presents an AFM phase image of poly1 cross-linked at 80% concentration for a dried sample. The image size is 1 μm × 1 μm, and the length scale of the observed structure is ∼27 nm, while an AFM image of a cross-linked homopolymer PEO shows no microstructure under similar conditions.

III. PCL Degradation from Cross-Linked PCL-*b*-PEO-*b*-PCL. PCL was removed from the networks to produce nanostructured and porous PEO hydrogels. Ester linkages in the PCL blocks were degraded by hydrolysis in a NaOH(aq) solution, as shown in Scheme 2. The hydroxyl functional groups of PEO are restored following PCL removal.

FTIR was used to probe the absence of PCL in the degraded sample. As shown in Figure 7, the sample after the PCL degradation shows complete loss of the PCL-unique C═O peak at 1726 cm^{-1}. The weight loss after degradation of PCL supports this conclusion. As shown in Figure 8, poly3 is 44 wt % PCL, and the measured weight losses of 46−51% suggest the complete removal of PCL with nearly complete retention of the PEO during degradation.

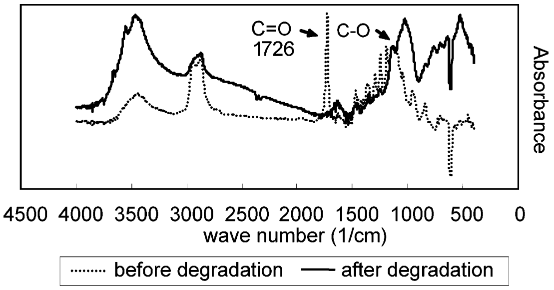


Figure 7. FTIR of poly3 before and after PCL removal.

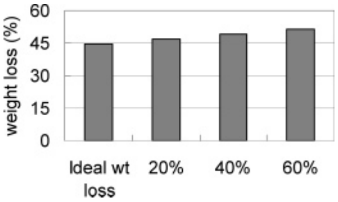


Figure 8. Weight loss after PCL degradation (poly3); 20%, 40%, and 60% denote samples that were cross-linked at 20%, 40%, 60% polymer concentrations followed by PCL removal.

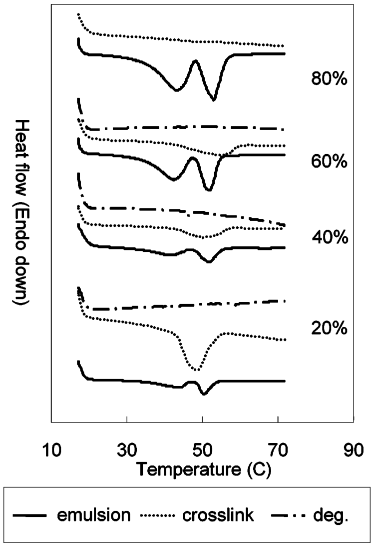
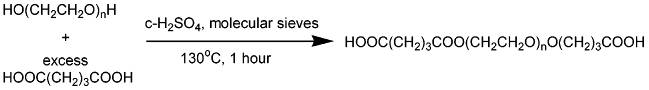


Figure 9. DSC of poly1 before and after cross-linking and after PCL degradation; in emulsion data, the first peak at around 44 °C corresponds to the T_m of PEO, and the second at 53 °C is that of PCL.

DSC results for poly1 in aqueous solution, after cross-linking, and after PCL degradation further confirm this picture of the synthesis process: microphase separation in water, PEO cross-linking, and PCL removal. As shown in Figure 9, some crystallinity of both the PEO and PCL blocks remains in aqueous "emulsions", which at higher polymer concentrations more resemble "pastes". The presence of two peaks indicates microphase separation. The lower of the peaks at 44 °C is identified with PEO, in agreement with observed melting points in the presence of water for a homopolymer PEO sample, $M_n = 15\,000$ g/mol, with values of 50 °C at polymer concentrations of 20%, 40%, 60%, and 80% (data not shown). The T_m of a PCL homopolymer, $M_n = 8000$ g/mol, was reported to be 55 °C,[19] and thus the second, higher peaks in the DSC curves at 53 °C

Scheme 3. Esterification of the Nanostructured and Porous Hydrogel with Glutaric Acid



$$\mathrm{HO(CH_2CH_2O)_nH} + \text{excess } \mathrm{HOOC(CH_2)_3COOH} \xrightarrow[\text{130°C, 1 hour}]{\text{c-}H_2SO_4\text{, molecular sieves}} \mathrm{HOOC(CH_2)_3COO(CH_2CH_2O)_nO(CH_2)_3COOH}$$

are identified with the PCL domains. Since crystallization of PEO is affected by the presence of PCL, the T_m of PEO is expected to decrease from the homopolymer value in triblock copolymers.[24] As the polymer concentration is reduced, the lower, PEO peak becomes less intense, relative to the PCL peak, due to the increased local presence of water in the PEO domains. In addition, wet samples after cross-linking and PCL removal were studied by DSC as well (Figure 9). Following cross-linking, the PEO peak is further reduced. Following degradation, the PCL peak is lost as well.

The nanostructured and porous PEO hydrogels were investigated with SAXS in the swollen state; however, no scattering peaks were observed following PCL removal. As this could occur if the length scales of the porous structures in the swollen hydrogels were beyond the detection limit of the SAXS apparatus, USAXS experiments were performed, but these as well showed no significant structure. Any "porous" hydrogel swollen in a good solvent (here water) has solvent everywhere, and the "pores" are defined as those regions in which there are no spanning polymer chains, which themselves constitute a minor component even in the "nonpore" regions. Thus, another possible explanation of the lack of observed structure in the SAXS spectra is a small contrast between "pores" and "matrix". SANS experiments in heavy water are intended to provide greater contrast. Another explanation is that following PCL removal, the PEO further swells to reduce spatial heterogeneity. But even if this were the case, the resulting hydrogels yet may have interesting macromolecular transport properties due to the necessarily inhomogeneous distribution of cross-links. There may exist "breathing modes" in which the hydrogel opens an O (10 nm) void corresponding to the initial location of a PCL-rich domain, such that there are little or no PEO strands crossing the void to entangle a passing macromolecule. A study of transport properties is underway and will be the subject of a future publication.

IV. Esterification of the Nanostructured and Porous PEO Hydrogel. After PCL removal, the terminal hydroxyl groups of PEO are restored and become available for further chemical modification, providing new functional groups localized to the former domain boundaries. To confirm this, the porous PEO hydrogel produced by PCL degradation from poly3 was reacted with an excess of glutaric acid. The procedure is shown in Scheme 3. FTIR spectra of the reacted hydrogels following extraction show that ester groups are produced during this process. As shown in Figure 10, the presence of a C═O stretch at 1728 cm^{-1} and a hydrogen-bonded O−H stretch originating from carboxyl groups of the glutaric acid on the reacted hydrogel indicate that the hydroxyl groups at PEO termini are chemically available. For samples exposed to similar conditions but lacking the glutaric acid, these signs of ester formation are not evident. If these hydroxyl groups are used to attach environmentally responsive materials, the pores may be further controlled by pH or temperature, which would be useful in biological applications such as drug delivery.

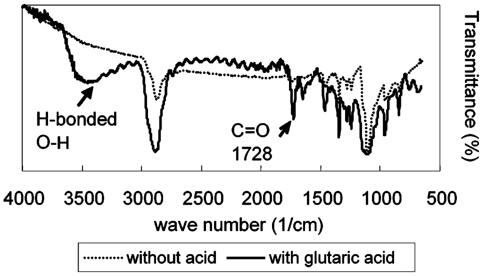


Figure 10. FTIR of the nanostructured and porous PEO hydrogels after treatment in esterification reaction conditions with (solid line) and without (dotted line) glutaric acid.

Conclusion

Nanostructured and porous PEO hydrogels were synthesized using amphiphilic PCL-*b*-PEO-*b*-PCL triblock copolymers. After microphase separation of the triblock copolymers in water, cross-linking of the PEO block was performed with an electron beam, followed by PCL removal through hydrolysis. Microphase structures were observed by SAXS (emulsion samples) and AFM (cross-linked samples); they were mostly lamella yet cylindrical in one instance. SAXS experiments following PCL removal showed no significant structure, perhaps due to a lack of contrast in swollen states of the "porous" hydrogels. To further investigate these materials, SANS and macromolecular transport experiments are planned. These nanostructured and porous hydrogels have hydroxyl functional groups available for further chemical modification and can be used in biomedical or pharmaceutical applications.

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